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Research Article

Removal of Lead (II) Ion from Aqueous Solution by Adsorption unto Chitosan Polymer

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Abstract

The adsorption efficiency of chitosan for Pb^{2+} ion was investigated for various concentrations of the metal ion solution at different time and at various temperatures. The Chitosan displayed good adsorption properties of the metal ion. FTIR study revealed that the major shifts in the frequencies of adsorption. New bonds were formed at 1411, 2262 and 3759 cm^{-1} while N-H and C-O bond at 1587 and 1320 cm^{-1} respectively. The new and missing bonds were assumed to be directly involved in the absorption of lead ion onto chitosan surface.

Key Words: Heavy metal pollution, lead ion, remediation, adsorption, chitosan.

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Introduction

Water pollution is an endemic problem because it is generated at a source (where wastes are discharged) but widely transported to several locations and has the potential of affecting the entire ecosystem. Industrialization is the earnest expectation of a developed and developing nation. However, industrialization releases several pollutants to the environment, which implies that the discharge of waste should be properly monitored. A cardinal point in waste disposal is to reduce the toxic components of a given waste to permissible value. Heavy metals are common industrial

waste and their disposal to water bodies can affect the quality of the water, aquatic animal and even man through bioaccumulation.

Adsorption is one of the most effective methods available for the removal of heavy metals from aqueous solution. Adsorption involves the use of suitable adsorbent through which the metal ion will be adsorbed onto the surface by physiosorption or chemisorptions mechanism. Several adsorbents have been reportedly used for the removal of heavy metals from aqueous solution but some of the adsorbents are less effective, some are non-biodegradable while other are expensive. The present study is aimed at using chitosan to remove lead (II) ion from aqueous solution. The application of biopolymers such as chitin and chitosan is one of the emerging adsorption methods for the removal of heavy metal ions, even at low concentrations (Crini, 2006). Chitosan is a natural polyaminosaccharide, synthesized from the deacetylation of chitin, a polysaccharide consisting predominantly of unbranched chains of -(1→4)-2-acetoamido-2-deoxy-d-glucose. Chitin is the second most abundant polymer in nature after cellulose. It can be extracted from crustacean shell such as prawns, crabs, fungi, insects and other crustaceans Wan *et al*., (2000). It is an established fact that chitosan exhibits natural support for enzyme immobilization because of its special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, adsorption properties, etc (Kumar, 2000). Chitosan can be used as an adsorbent to remove heavy metals and dyes due to the presence of amino and hydroxyl groups which are active functional groups for adsorption (Wu et al., 2001). The chemical structure of chitosan is shown in Fig 1.

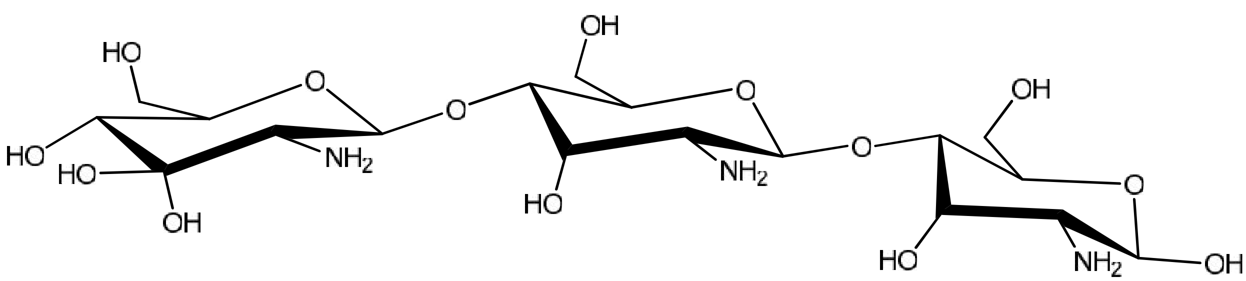

Fig 1: Chemical structure of chitosan

Several works on adsorption of heavy metals using chitosan or modified chitosan polymers have been reported. Some of them are graft copolymerization of polyacrylonitrile on the chitosan surface in the presence of ceric ammonium for the removal of Cr (VI) and Cu (II) ions from aqueous media (Shanmugapriya *et al*., 2013). Thiourea modified chitosan for the adsorption of Hg (II) (Hritcu *et al*., 2012). Beads of

thiourea-modified chitosan used for the adsorption of Cu (II) was prepared by several media (citric acid, sodium hypophosphite, glutaraldegyde, and SiO_2) (Benavente *et al*., 2011). Graft copolymerization of chitosan with polyacrylonitrile in the presence of ceric ammonium nitrate used for the removal of Pb (II) and Ni (II) ions from aqueous solutions (Repo *et al*., 2011). In order to facilitate the adsorption efficiency, Shanmugapriya *et al*. (2011) combined chitosan with sodium alginate for the removal of Cu (II), Cd (II), Pb (II) and Ag (II) ions from waste water.

The Cu (II) and Ni (II) ions were removed from metal solution by using crosslinked chitosan synthesized by graft copolymerization of chitosan with acrylonitrile in presence of ceric ammonium nitrate as initiator. Adsorption of Lead (II) ion on chitosan has found to be dependent on contact time, concentration, temperature, and pH of the solution (Chiou *et al*., 2004; Wu et al., 2001).

The aim of the study was to investigate the adsorption efficiency of chitosan for Pb^{2+} ion at various concentrations of the metal ion solution at different time and at various temperatures.

Materials and methods

Chitosan sample was supplied by Prof. Lee Wills, a Professor in the Department of Chemistry, University of Saskenchewan, Canada. Batch experiments were carried out as reported elsewhere to investigate the effect of concentration on the adsorption of various concentrations of lead by chitosan. The wavelength of maximum absorption of lead was determined using Pye Unicam Atomic Absorption Spectrophotometer and this wavelength was used for subsequent analysis after the preparation of calibration curve. Concentration of lead adsorbed was calculated using the following equation, FTIR analysis of the samples (chitosan before and after adsorption of lead ion) was carried out using FTIR spectrophotometer. The samples were prepared using KBr powder and the scanning was done in the range of 450 to 500 cm.

Results and Discussions

Adsorbance study

The adsorption of lead ion from aqueous solution has been found to depend on a number of factors, including period of contact, pH, temperature, mass of the adsorbent, concentration of the adsorbate, particle size, etc. However, in this work, the only effect of temperature, contact time and concentration of adsorbate was investigated.

Spectrophotometric method was used for analysis of the solution containing unadsorbed lead ions. The implication is that the difference in adsorbance before and after adsorption is an indication of the amount of lead ion that is adsorbed. This is because, according to Beer-Lambert law, absorbance is directly proportional to concentration, ie,

$$A = \varepsilon l C \qquad 1$$

Where A is the adsorbance, l is the path length of the sample cuvette (which is constant) and C is the concentration of the analyte. The mathematical significance of the equation is that a plot of A versus C should give a straight line passing through the origin, whose slope is equal to ε, the molar absorptivity (since in most cases l is always equal to unity). From the above, it is conventional that the adsorbance of the solution containing unadsorbed lead ions will decrease as the concentration of lead ion adsorbed increases and vice versa. Therefore, this study presents a preliminary method for evaluating the extent of adsorption of lead ions on chitosan at various temperature, time and concentration. Fig. 2 shows plots for the variation of adsorbance with concentration for solution containing various concentrations of lead ions.

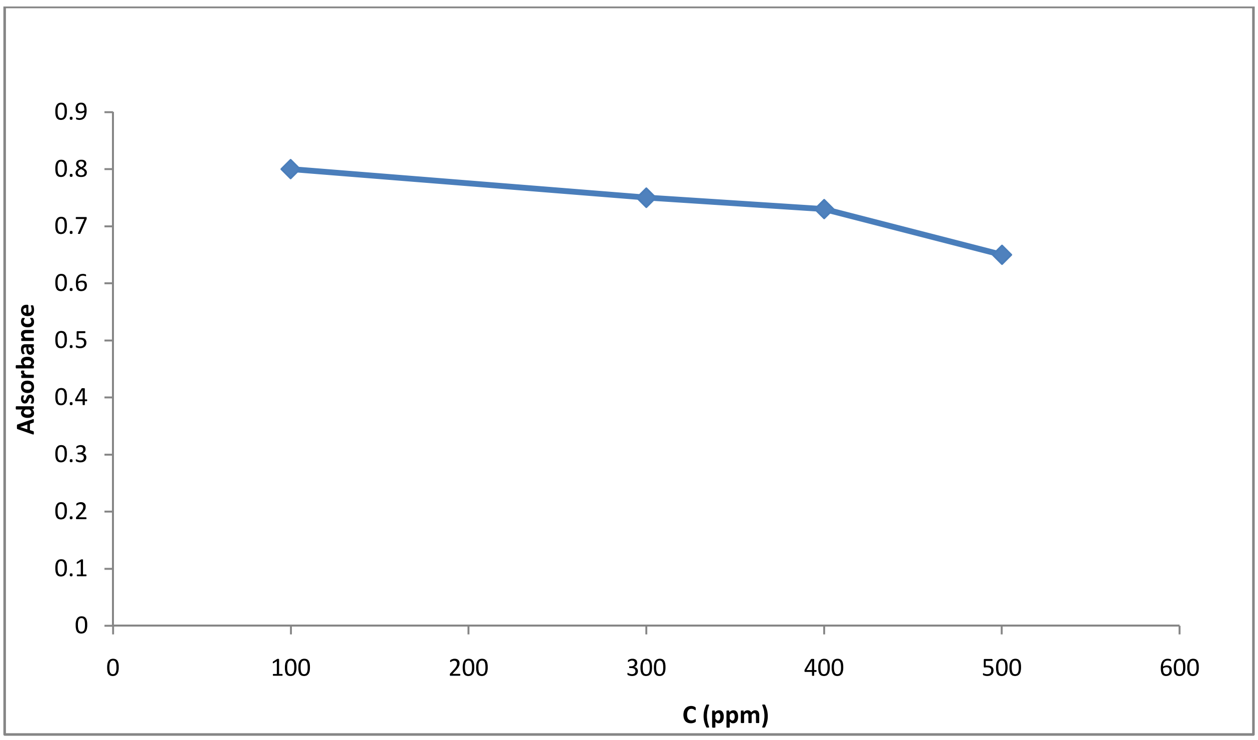

Fig. 2: Variation of adsorbance with initial concentration of Pb^{2+}

The adsorbance is seen to decrease with increase in concentration indicating that the concentration of lead ion unadsorbed decreases as the concentration of adsorbed lead ion increases. Increase in the amount of heavy metal ion adsorbed with concentration is an indication that the adsorption process is effective. As the concentration of the solution increases, the amount of lead ion in the solution increase, the probability of sticking also increases hence the Observe trend.

In order to investigate the effect of time on the adsorption of Pb^{2+} by chitosan, adsorbance of 500 ppm solution of the heavy metal ion (in contact with the adsorbent at various time) were measured. The data obtained were used to develop the plot given in Fig. 2.

The graphs reveal that the adsorbance first increases and then decreases with time. The initial increases correspond to the point where the amount of Pb^{2+} adsorbed is minimum while the progressive decreases indicate that the amount of lead ion adsorbed increases with time. An increase in the amount of adsorbate with time is due to the fact that as the period of contact increases, the tendencies of the adsorbate to be adsorbed increases until all the vacant adsorption sites are completely covered. The results obtained suggest that the best adsorption efficiency of chitosan for Pb^{2+} will be time dependent. Therefore, optimum performance of chitosan as an adsorbent for lead ion can be achieved by taking advantage of background factors, including time.

Fig. 3 shows a plot for the variation of adsorbance of solution containing unadsorbed lead ion with temperature. The plot reveals that the adsorbance of the solution decreases with temperature. This implies that as the temperature increases, the amount of lead ion adsorbed by chitosan also increases. The observed trend suggests that the adsorption of lead ion on the surface of chitosan is consistent with the mechanism of chemical adsorption. In chemical adsorption, the extent of adsorption increases with increase in temperature, whereas in physical adsorption, the extent of adsorption decreases with increase in temperature.

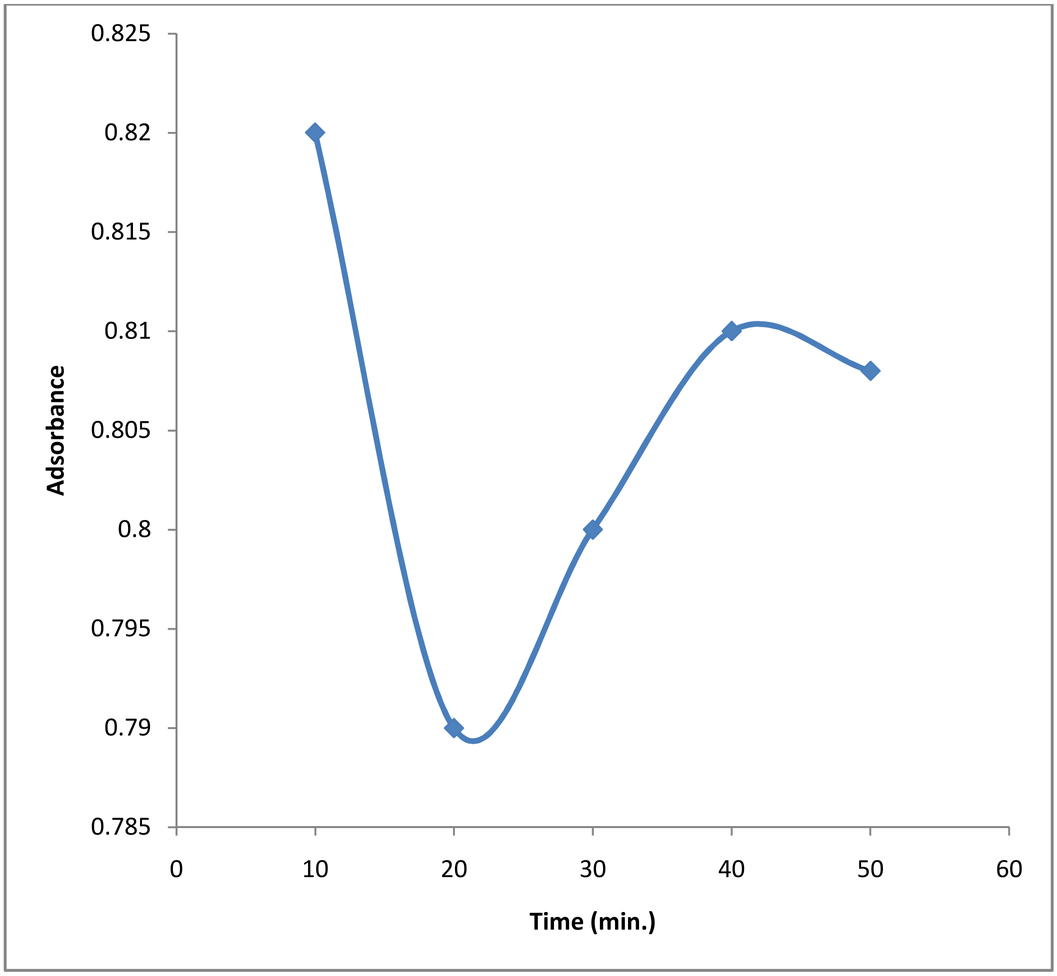

Fig. 3: Variation of absorbance of solution of unadsorbed Pb^{2+} with concentration

Temperature can exert several significant impacts on the surface properties of an adsorbent. At high temperature, the adsorbent may be activated, charged or modified in such a manner that the number of adsorption site increases or become more active. Temperature can also modify some functional groups in the chitosan and encourage better adsorption.

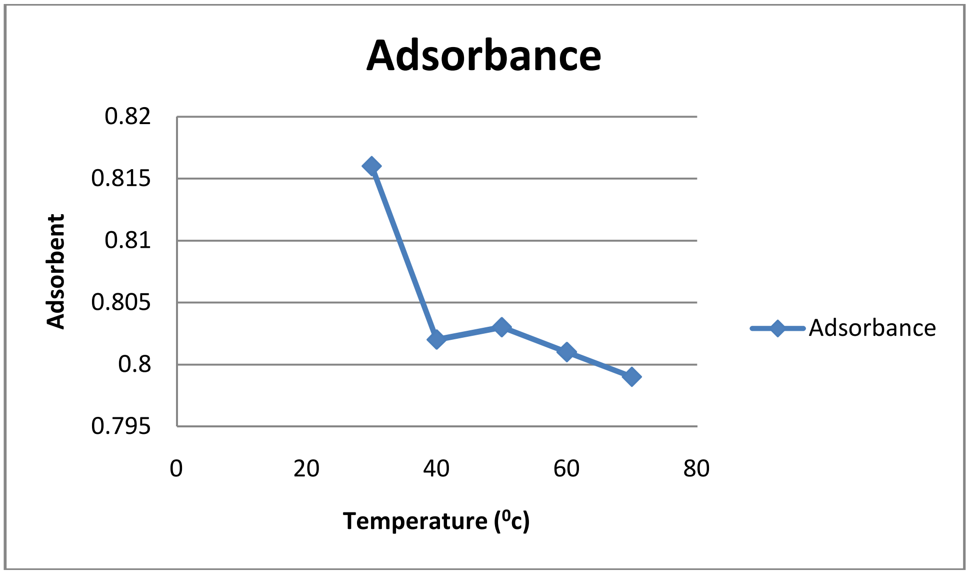

Fig. 4: variation of adsorbance of solution of unadsorbed Pb^{2+} with temperature

FTIR study

Fig. 4 shows the FTIR of pure chitosan while the peaks and the frequency of adsorption are shown in Table 1. From the results obtained, the main functional groups or vibrations associated with chitosan are the C-N stretch at 1082 cm^{-1}, N-H bending vibration at 1587 cm^{-1}, C=C stretch at 1649 cm^{-1}, C-H stretch at 2890 cm^{-1} and OH stretch at 3385 cm^{-1}. After adsorption of lead ion by chitosan, the spectrum obtained is shown in Fig. 5 and 6 while the peaks and frequencies of adsorption are recorded in Table 2.

C-N stretch shifted from 1082 to 1040 cm^{-1} with increase intensity and increasing area. C=C stretch shifted from 1649 to 1547 cm^{-1}, C-H stretch at 2890 shifted to 2903 cm^{-1} and OH stretch at 3385 shifted to 3422 cm^{-1}. New bonds were formed at 1411, 2262 and 3759 cm^{-1} while N-H and C-O bond at 1587 and 1320 cm^{-1} respectively, were missing. Interestingly, the shift between 1082 and 1649 cm^{-1} occurred with increasing intensity suggesting better bond compartment through adsorption. Generally, shift in frequency after adsorption agrees with the existence of interaction between the adsorbent (chitosan) and the adsorbate (lead ion) while the appearing of new bond suggests the point of adsorption facilitated by the missing bond.

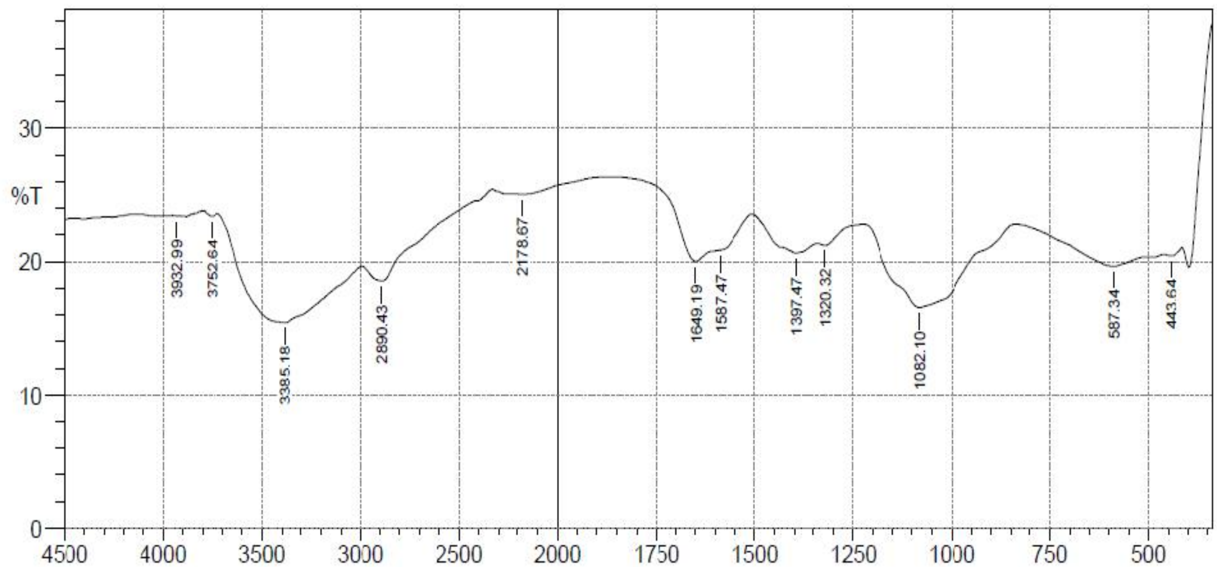

Fig. 5: FTIR of chitosan

Table 1: Frequencies and peaks of FTIR spectrum of chitosan

Frequency	Intensity	Area	Assignment	
1082	17	276	C-N stretch	Amine
1320	21	76	C-O stretch	Alcohol, carboxylic acid, ether, esther
1587	21	54	N-H bend	Amine
649	20	133	C=C	Alkene
2890	19	387	C-H stretch	Alkane
3385	15	253	OH stretch	Alcohol, phenol

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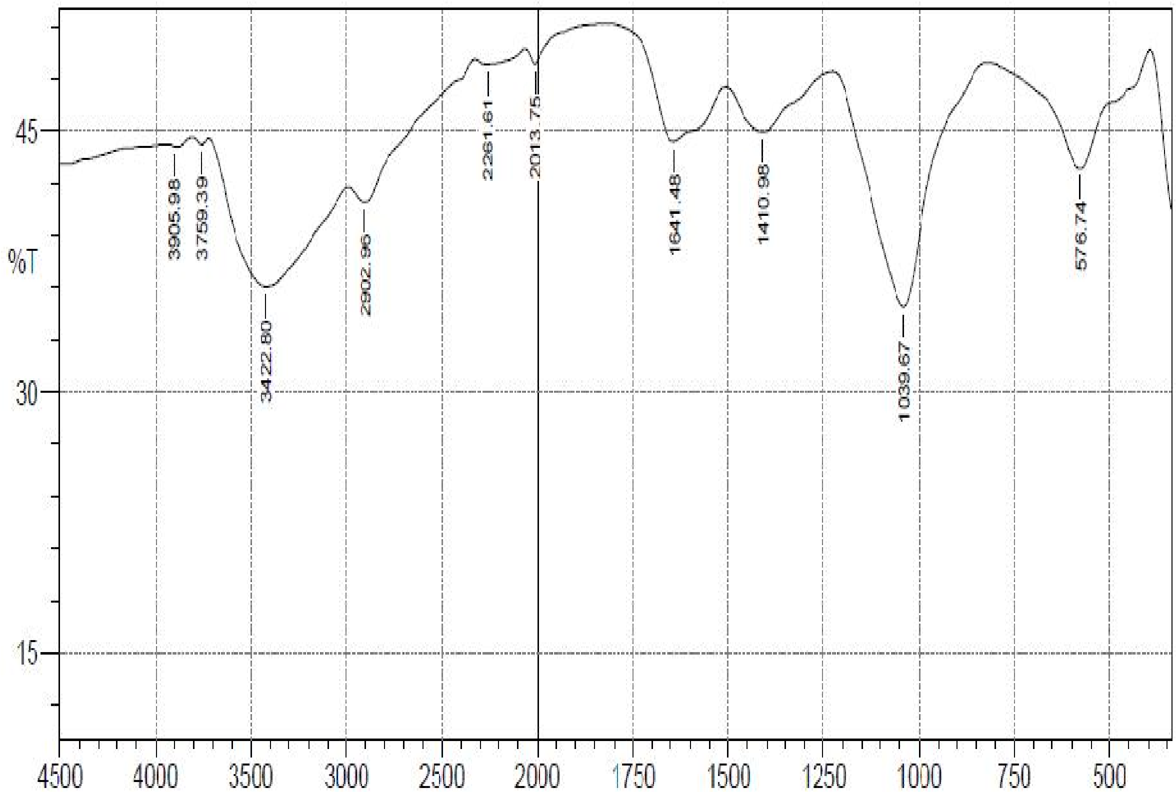

Fig. 6: FTIR of chitosan after adsorption of Pb^{2+}

Table 2: Frequencies and peaks of FTIR spectrum of chitosan after adsorption of Pb^{2+}

Frequency	Intensity	Area	Assignment	
577	43	142	C-X stretch	Alkyl halide
1040	34	150	C-N stretch	Amine
1411	45	63		
1642	44	101	C=C	Alkene
2014	49	60		
2262	49	81		
2903	41	231	C-H stretch	Alkane
3422	36	122	OH stretch	Alcohol, phenol
3759	44	25		

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Conclusion

The results and findings obtained from the study on the removal of lead ion from aqueous solution, leads to the following conclusions;

i. Chitosan is a good adsorbent for Lead ion from aqueous solution.
ii. The adsorption capacity of chitosan for lead ion increases with increase in concentration.
iii. The adsorption capacity of chitosan for lead ion increase with increase in temperature, which suggest the mechanism of chemical adsorption.
iv. The adsorption of lead ion on chitosan can be optimized for better efficiency by taking advantage of time, concentration and temperature.

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